STUDY OF ELECTROLYTIC DISSOCIATION IN IODIC ACID BY RAMAN EFFECT *

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ABSTRACT The present work is an attempt at studying the electrolytic dissociation in iodic acid by Raman Effect on the same lines as is done in the case of nitric acid and sulphuric acid by the author. Iodic acid is found to contain polymerised molecules of the type $(HIO_3)_2$ in concentrated solutions. As the acid is diluted, the polymers are found to dissociate into HIO_3 molecules which again dissociate into IO_3 ions at still lower concentrations. On comparing 0.1N solutions of KIO_3 and HIO_3, it is found that the intensity of IO_3 line in KIO_3 solution is much larger than in HIO_3 solution. It is concluded that the acid is not completely dissociated even in such a dilute solution.

INTRODUCTION

In a previous communication,[1] the author made a quantitative study of electrolytic dissociation in sulphuric acid. The present work is an attempt at a similar study in iodic acid. Iodic acid has been studied both in crystalline state and in solution by many workers including Krishnamurty,[2] Nayar and Sharma,[3] Nayar and Gairola,[4] and Woodward.[5] The latest work is that of Venkateswaran[6] who made a study of the acid in many of its aspects. The interpretation of the results by various authors are conflicting. Woodward thinks that the acid is highly dissociated even in concentrated solutions and in fact Krishnamurty[2] and Shen, Yao and Wu[7] discussed the structure of IO_3 ions by assuming that a solution of iodic acid of 5N concentration is completely dissociated. On the other hand, Venkateswaran[6] maintains that the acid is very weak and undissociated molecules are found even in dilute solutions. Venkateswaran's observations are based on visual estimate of the structure and positions of the maxima of the wide bands of the acid at various concentrations. The author, from a study of the microphotometric records of the spectra, found discrepancies between the Raman frequencies of the maxima of the bands reported by Venkateswaran and those observed by the author. Also, the structures of the bands observed by

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Venkateswaran and those revealed by the microphotometric records were found to be different.

EXPERIMENTAL

Pure crystals of Iodic acid supplied by Merck are taken and dissolved in double-distilled conductivity water and filtered through a cintered glass crucible avoiding the use of any filter paper, lest the filter paper should be acted upon by the acid thereby contaminating it. Aqueous solutions of concentrations 18N, 15N, 12N, 6N, 3N, 1N, 1.6N, 0.8N, 0.4N are made. A solution of KIO_3 is made by dissolving pure crystals in pure water. This solution is treated with pure carbon while hot and filtered through a cintered glass crucible using a quantitative filter paper. This method is found to be very effective in purifying the solution from fluorescent and colloidal impurities.

The arrangement used to photograph the Raman spectra is the same as in the case of sulphuric acid by the author. In the case of very dilute solutions where very long exposures are needed to bring out the weak Raman lines with sufficient intensity the problem of the superposed continuous spectrum becomes very acute. Therefore, a double-jacketed Wood's tube is employed, so that two filters—iodine in carbon-tetrachloride and a saturated solution of $NaNO_2$—could be used to isolate the 4358 line of the mercury arc for exciting the Raman lines. The solution of $NaNO_2$ is replaced, every time the solution in the Wood's tube is replaced, so that the filter may not, owing to photochemical decomposition and development of colour, diminish the intensity of the exciting radiation. In the case of concentrated solutions, *viz.*, 18N, 15N, 12N, and 6N, equal exposures of one hour each are given. Solutions of concentrations 6N, 3N and 1N and 1.6N, 0.8N and 0.4N are exposed for periods proportional to dilution in two sets of three concentrations each.

An exposure of one hour was sufficient to bring out the Raman spectra of crystalline HIO_3 and KIO_3. To study the solution of iodic acid at higher temperature, the Wood's tube was sealed and enclosed in a steel tube with a slot cut on its side to allow the light from the mercury arc condensed by a large double condenser to fall on the Wood's tube. A current of about 2 amperes was sent through the heating coil wound on the steel tube to heat the tube inside. Thus a temperature of 130°C. could be attained. The spectra at 30°C. and 130°C. are compared.

RESULTS

The Raman frequencies of the maxima, in the crystals and in solutions of iodic acid and KIO_3, are given in the following table. Besides the frequencies reported in this table many low frequencies are found in the spectra of the crystals. But they are very feeble and are found to be absent in solutions.

TABLE I

HIO_3-crystal		18N		15N		12N		6N		3N		1N		0 5N	
1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
328	331	334	326	—	324	334	324	330	324	328	324	—	324	328	—
377	376	463	—	—	—	463	—	—	—	—	—	—	—	—	—
633	636	644	640	—	640	644	636	644	636	644	—	—	—	644	—
713	728	779	772	—	770	796	796	796	796	798, 796	803	—	810	802	—
782	788	—	—	—	—	—	—	789	—	—	—	—	—	800	—
—	—	823	—	—	—	823	—	823	—	823	—	—	825	819	—

TABLE II

HIO_3	1.6N	0 8N	0.4N	KIO_3 0.4N	KIO_3 1N	$LiIO_3$ 3.4N	$LiIO_3$ 2.3N	$LiIO_3.HIO_3$ 1.15N	KIO_3-crystal	
2		2	2	2	1	1	2	2	1	2
324		324	324	324	333	320	324	324	132	—
									308	—
—		—	—	—	—	423	—	—	335	—
									341	—
—		—	—	—	—	603	636	636	737	742
									753	761
810		810	810	810	803	794	810	810	789	795
									808	812
825		825	825	—	—	—	—	—		

In the above Tables the frequencies given under the column 1 are due to Venkateswaran and those under the column 2 are due to the author.

From the above tables, it is clear that there are large differences in the frequencies of the maxima of the Raman lines between those reported by Venkateswaran and the author. This should be attributed to the errors in visual judgement in the location of the maxima in Venkateswaran's pictures. The band at 636 is found in all the spectra, but in dilute solutions it is very weak and diffuse and therefore its maximum could not be correctly located.

STRUCTURE OF THE BANDS

The sharp lines 331 and 376 of crystalline iodic acid shift to a lower frequency and broaden out (see the photometric records) to form a band with its maximum

at 324. This band appears with medium intensity in all the spectra, with varying structure and gets diffuse in the intermediate concentrations. But in the dilute solutions again, the band becomes narrower.

The line at 636 in the crystalline iodic acid gives rise to a diffuse band in the solution. This band appears with medium intensity in concentrated solutions but rapidly gets feebler and diffuse, but continues to persist even in very dilute solutions. This is found to be present even in solutions of iodates, especially in the solution of $LiIO_3$ of concentration 2.3N.

Venkateswaran reported a feeble band 463 which fades off with dilution. It is found in the pictures taken by the author.

The bright and sharp lines 728 and 788 of the crystal shift to higher frequency and diffuse out to give a bright diffuse band with its maximum at 772 in the 18N solution. It undergoes conspicuous changes with dilution. Venkateswaran describes that this band has a high-frequency component which gets feeble and gradually dies out with dilution, while the main band gets weaker and diffuse on dilution and in the solution of 6N it is superposed upon by a sharp line. This line becomes stronger at the expense of the band as the concentration is further decreased still at very low concentrations, the band disappears leaving a strong sharp line. He found a line 823 corresponding to the high-frequency component of the main band in the spectrum of crystalline $KIO_3.HIO_3$ and therefore attributed this to the I_2O_6 ions. He suggested that the strong line is due to the IO_3 ions formed due to the dissociation of the HIO_3 molecules represented by the main band.

But the photometric curves of the author reproduced in Fig. 1 give a different result. The main band has an unsymmetrical structure in the concentrated solutions, and its maximum gradually shifts to higher frequency from 15N. In the 3N solution, the band is shifted to 803 and assumes a symmetrical structure. At still lower concentrations it splits up into 2 lines, 810 and 825, of which 825 gets feebler and feebler and 810 gets more and more intense with dilution. This behaviour of the band can be looked upon as due to the superposition of 2 components, with their maxima at about 770 and 825 of the crystal corresponding to the lines 728 and 788 which shift to higher frequency from crystal to solution. As the concentration is decreased, the component 770 gets feeble until at 1N it is practically absent, while the component 825 gets brighter at the expense of its neighbour. As a result of blending of these bands into each other, the maximum of the resultant appears to shift to higher frequency. At still lower concentrations 1N, another line at 810 makes its appearance, while the band 125 is reduced to a feeble line at 825, which goes on diminishing in intensity on dilution while 810 is getting brighter, as is already described.

Effect of Temperature. Spectra of the acid of concentration 18N taken at the laboratory temperature and at a temperature 130°C. are compared to see if there are any changes in the structure, which would help to study its properties

better. But the changes are found to be very slight and cannot be described accurately, though the range of temperatures is large. It could not be studied at still higher temperatures as the acid is found to decompose slightly.

DISCUSSION

The changes in the structure of the bands with dilution can be interpreted on assuming the presence of three kinds of molecules $(HIO_3)_2$, HIO_3 and IO_3, $(HIO_3)_2$ and HIO_3 being predominent in the concentrated solutions and HIO_3 and IO_3 in the dilute solutions. The band at 324 is the result of superposition of three bands excited by the three types of molecules. They are very close to each other and therefore the changes that each component undergoes on dilution cannot be traced.

Nayar and Sharma, attribute the band 636 to the $(HIO_3)_2$ molecules as the band gets feebler on dilution and could not be photographed by them in the dilute solutions. Venkateswaran [6] refuted the above contention as he found it in his spectra of dilute solutions also. The two conflicting views can be explained if it is assumed that this band is the resultant of the bands excited by $(HIO_3)_2$, HIO_3 and IO_3, and that the contribution to the intensity of this band due to $(HIO_3)_2$ is large compared to that due to HIO_3 or IO_3. With decreasing concentration $(HIO_3)_2$ molecules dissociate into HIO_3 and therefore the intensity of the band falls off more than in proportion to dilution.

The behaviour of the band 770, which is the most intense of all, also can be ragarded as due to the superposition of the bands excited by $(HIO_3)_2$ and HIO_3 and in dilute solutions by IO_3 ions. The component with the maximum at 770 is due to $(HIO_3)_2$ molecules and that at 825 to HIO_3 molecules. With decreasing concentration $(HIO_3)_2$ molecules dissociate to HIO_3 molecules and hence the 770 band is decreasing in intensity while 825 is increasing in intensity on dilution, the resultant of the band thus appearing to shift towards 825. 3N downwards, $(HIO_3)_2$ molecules are absent and HIO_3 molecules, which are predominent, begin to dissociate to IO_3 and H and the line at 810, due to IO_3 ions, becomes progressively intense on further dilution.

In this connection, one point requires elucidation. Venkateswaran attributes the component 825 to I_2O_6 ions as this line is found in the spectrum of crystalline $KIO_3.HIO_3$. This view warrants a large dissociation of the acid even in high concentrations where the intensity of this line is large, which means a high electrical conductivity of the acid at those concentration. But the acid is considered to be very weak. Therefore the above contention is untenable.

It is possible to calculate roughly the degree of dissociation of the acid in the lower concentrations by comparing the intensity of the 810 line in the solutions of the acid and KIO_3, on the same lines as was done for H_2SO_4 studied by the author. The following table gives the intensities of the lines in solutions of the acid and KIO_3.

Solution	Intensity of IO_3 line 810	Degree of dissoc.
KIO_3 0.4N	353	100%
HIO_3 0.4N	199	56%
HIO_3 0.8N	140	40%

Concentrations of only those solutions for which the lines 810 and 825 are sufficiently resolved are taken. At higher concentrations the lines are diffuse and the intensities of the two components cannot be accurately determined. At still lower concentrations the lines are superposed by the background and therefore their intensities could not be accurately determined.

From the above table it is clear that, even at such concentrations as 0.4N, the degree of dissociation is only 56%. Even in dilutions of 0.1N of HIO_3 the intensity of the 810 line of HIO_3 is found to be smaller than that in 0.1N KIO_3 which indicates that the dissociation is incomplete even at that dilution. Therefore iodic acid should be regarded as a weak acid compared with nitric acid or sulphuric acid.

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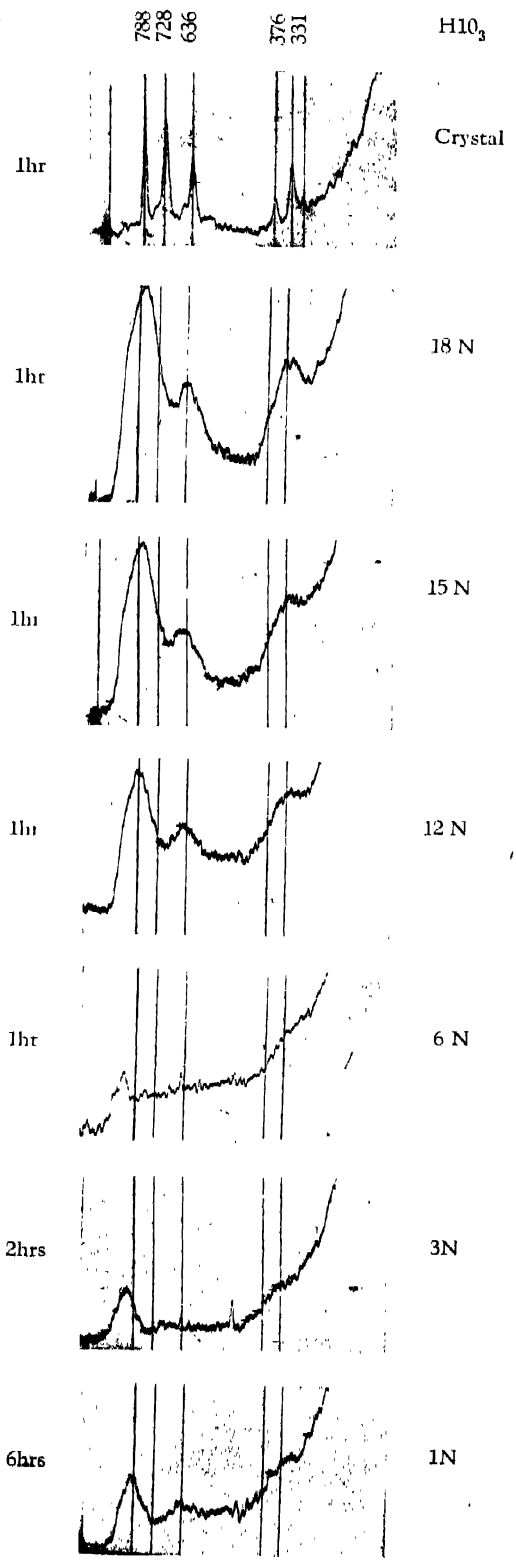
TIME OF EXPOSURE
788
728
636
376
331
HIO_3
1hr
Crystal
1hr
18 N
1hr
15 N
1hr
12 N
1hr
6 N
2hrs
3N
6hrs
1N